

EXTENDING THE LINEAR ELASTIC RESPONSE REGION OF FLAX FIBRE REINFORCED POLYMERS USING CHEMICAL TREATMENTS

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ABSTRACT

It has been shown that the interphase, located between the elementary fibres in a technical flax fibre, possesses a very low shear stiffness [1]. This can lead to sliding of the elementary fibres inside the fibre bundle which may contribute to the viscoelastoplastic response of the composite material during tensile loading. The fibres were subjected to several chemical treatments which aimed at increasing the degree of polymerisation (DP) of the biopolymers in the interphase and inside the elementary fibres. Of the investigated chemical treatments only ethanedial was found to significantly alter the mechanical behaviour of the composite.

INTRODUCTION

Natural fibres and especially flax fibres are referred to as a potential competitor for glass fibres due to their high specific stiffness and strength [2]. However, flax fibres and their composites show a viscoelastoplastic response to tensile loads which might pose a problem in certain composite applications. In the design of a part, the initial stiffness of the composite is often used in calculations but this is only valid up to limited strains.

It has been established by several authors that, at least a part of this behaviour, is most likely due to the internal reorganisation of the fibre microstructure [3]–[5]. During tensile loading of the fibre, the cellulose microfibrils reorient so that their microfibrillar angle decreases. This must be accommodated by the surrounding matrix of amorphous cellulose, hemicellulose and pectin. Another mechanism that could play a role is the deformation of the inter-elementary fibre interphase inside the technical fibre, which possesses a very low shear modulus. Therefore, tensile loading of the fibre may also induce sliding of the elementary fibres inside the bundle.

Chemical treatments aiming at an increase of the DP of the non cellulosic polymers (NCP's) inside the fibre may inhibit one or both of the above mechanisms by improving the mechanical properties of these NCP's.

MATERIALS AND METHODS

Materials

Unidirectional composite samples were produced with FlaxTape 200 supplied by Lineo. This is a stabilized, unidirectional flax fibre tape with an areal density of 200 g/m². The resin consisted of epoxy (Epikote LVEL 828) combined with a 1,2-diaminocyclohexane hardener

(Dytek DCH-99). The ratio of resin to hardener was 100 to 15.2 on weight basis. The thickness of all composite samples was 2 mm resulting in a fibre volume fraction of 35%.

Various chemical treatments were applied to the UD flax tape, aiming at a crosslinking of the fibre's amorphous components. A 3wt% and 15 wt% solution of ethanedial, also known under its trivial name glyoxal, in water was mixed with a lewis acid catalyst $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ until the molar ratio aluminium sulfate/glyoxal was 0.04. The immersion of the fibre layers was followed by a heating step in which the fibers were heated to 160°C for 10 min. A second and separate treatment consisted of a 10 vol% 3-aminopropyltriethoxysilane (APS) solution in water, subsequently followed by a heating step of the fiber layers to 90°C for 1 hour. Finally, a 20 vol% dimethyloldihydroxyethylene urea (DMDHEU) solution in water was prepared. Immersion of the fibers in this solution was also followed by a heating step of 10 min at 160°C. After treating and heating, the fibre layers were rinsed in water to remove the possible excess of reactants.

Methods

Tensile tests were carried out in accordance with the ASTM D3039/D3039 M – 08 standard. Tensile specimen thickness and width were 2 mm and 12.7 mm, respectively. An Instron 4467 was equipped with a load cell of 30 kN. The total test span was 15 cm with an effective gauge length of 5 cm monitored by the extensometer. End tabs (glass/epoxy) with a taper angle of 90° were glued to all test specimens. Prior to testing, all samples were conditioned at 50% relative humidity at 20°C for at least 7 days.

X-ray photo-electron spectroscopy using a Surface Science Instruments SSC 100/206 spectrometer equipped with a micro-focussed and monochromatized $\text{AlK}\alpha$ x-ray beam enabled identification of functional groups present at the surface of the fibres.

Nuclear magnetic resonance (NMR) measurements were carried out using a Bruker AMX400 with a magnetic field strength of 7.0 T. Flax fibres were ground to produce a fine powder and pressed into 4 mm rotors. Cross polarization and magic angle spinning at a spinning frequency of 6 kHz was used to enhance the quality of the spectrum. 382 scans were accumulated with a recycle delay of 10 s. Contact time was 1 ms. Analysis and deconvolution was carried out with the dmfit program.

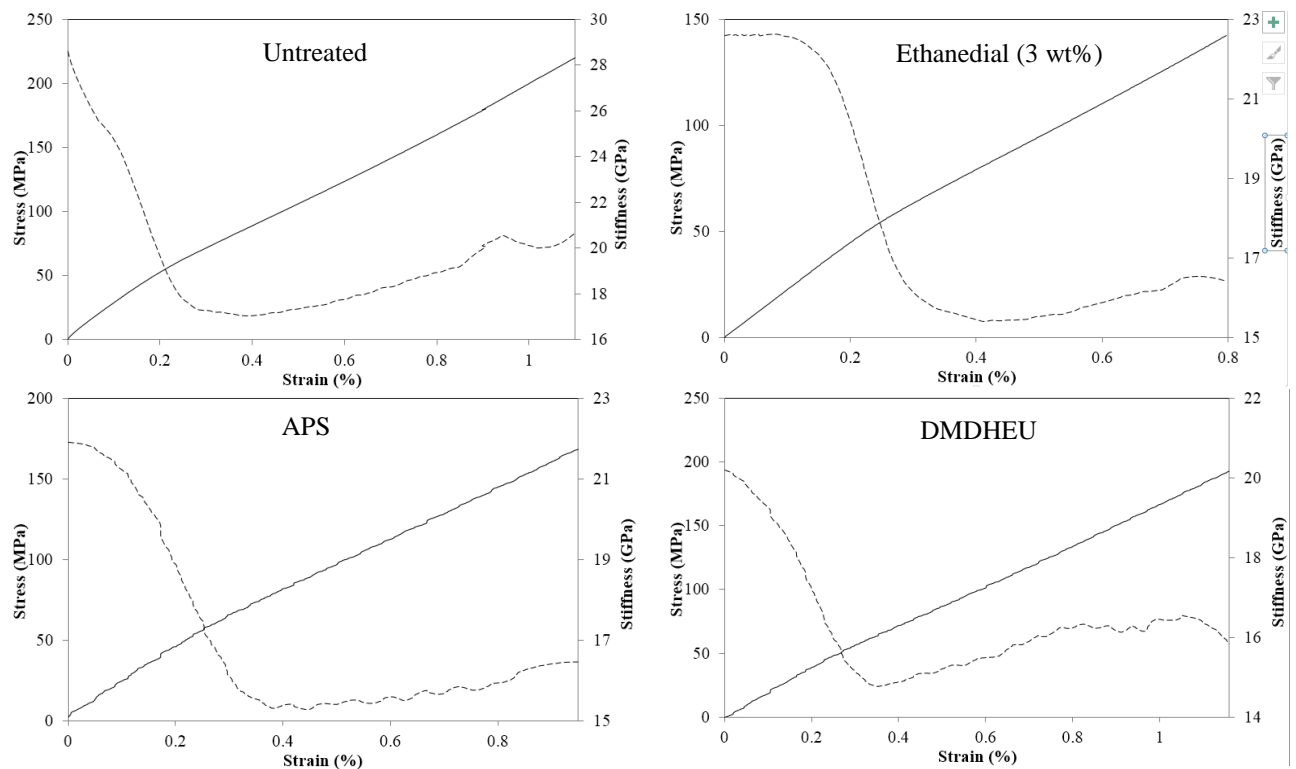
Fourier transform infrared spectroscopy (FTIR) was used to acquire infrared spectra of the fibres. A Bruker IFS 66v/S infrared spectrometer operating under high vacuum determined the absorption spectra for wavenumber between 400 cm^{-1} and 4000 cm^{-1} . Fibres were ground to a fine powder and diluted with KBr powder to enhance the transmission of infrared radiation.

RESULTS AND CONCLUSIONS

The stress-strain curve and tangent modulus for untreated and ethanedial treated (3wt% solution) fibres are shown in figure 1. The tangent modulus curve represents the numerical first derivative, based on the finite central difference method, of the stress-strain curve. A second order Savitzky-Golay filter was applied to the data to smoothen the resulting curve. When an untreated flax fibre composite is loaded in tension a quasi-immediate decrease in tensile modulus is noticed. As mentioned above, this could be due to the accommodation of the microfibrils' reorientation by the NCP's inside the elementary fibres or sliding of the elementary fibres relative to each other during deformation. The decrease continues until a minimum value is reached. At this point the stiffness of the composite has decreased by 25 to

30%, compared to the initial stiffness, i.e. the tangent stiffness at 0% strain. After this point the stiffness starts to recover but the recovery rate is slower than the degradation rate. This behaviour could be due to the reorientation effect becoming a dominant mechanism in the deformation process. Furthermore, crystallization of amorphous cellulose may also be present at this stage, as previously proposed by Placet et al. in hemp fibres [6]. Another possibility is that the NCP's between the elementary fibres may have reached a maximum flow point at which the polymer chains are too entangled or have aligned completely so that the load is carried by the primary bonds of the chains instead of the weak secondary van der Waals interactions between the chains.

Treating the fibres with ethanediol prior to resin impregnation extends the linear elastic region in the stress-strain curve of the composite. Significant results were obtained for 3 wt% and 15 wt% ethanediol treated fibres. Not only was the elastic region extended, the point at which the stiffness reached its minimum value was also shifted to slightly higher strain values. This could imply that the treatment has altered the chemical structure of the fibre so that a threshold stress value must be exceeded before the matrix is able to yield viscously. The treatment had no effect on the rate of degradation or recovery of the composite's stiffness. This supports the hypothesis that the treatment delays but not alters the mechanisms that occur in the composite containing untreated fibres. It is also seen that the 3 wt% and 15 wt% ethanediol treatments but especially the latter, embrittles the fibres. Indeed, when the NCP's in the elementary fibre or in the inter-elementary fibre interphase are stiffened and strengthened by creating crosslinks between the chains, stress concentrations will arise during microfibril reorientation which may lead to premature failure of these fibrils. The APS and DMDHEU treatment produced only a limited and inconsistent effect on the stiffness.



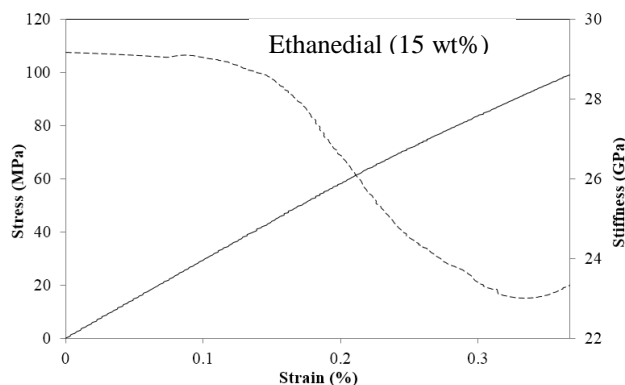


Fig. 1 Representative stress-strain curves (—) and tangent modulus (--) of untreated, ethanedial (3 wt%) treated, APS treated, DMDHEU treated and ethanedial (15 wt%) flax fibre reinforced epoxy [Unidirectional, $V_f = 35\%$].

Thus, it is hypothesized that ethanedial is able to form crosslinks between the different NCP's in the elementary fibre and the inter-elementary fibre interphase, thereby strengthening it. This is supported by the results of XPS (table 1) which show an increased amount of acetal, ether and ester bonds, indicating the formation of crosslinks. The same increases were also noticed on the surface of the APS and DMDHEU fibres but to a lesser extent. Note that it is impossible that the increase in these functional groups could have been caused by surface contamination of unreacted ethanedial, APS or DMDHEU since the XPS measurements are performed under ultra-high vacuum which would lead to the complete evaporation of the reactants considering their high vapour pressure.

Table 1: Mole percentages of the carbon atoms at the fibre surface ordered by the bonds in which they are involved. Results are obtained with XPS.

	C-C	C-O-C C-(O,N)	C=O O-C-O	O-C=O	Total
Untreated	60.5	18.3	4.8	1.4	84.9
Ethanedial	49.7	21.0	6.5	2.8	79.9
APS	53.2	20.0	5.3	1.5	80.0
DMDHEU	56.2	18.8	6.2	1.7	82.9

One possible reaction mechanism of ethanedial is elaborated in figure 2. The resulting acetal crosslinks should be stable and be able to withstand hydrolysis. However this was not verified experimentally.

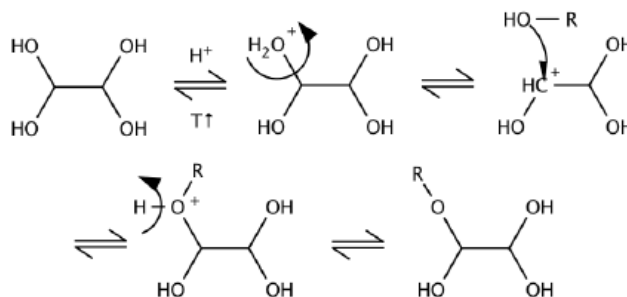


Fig. 2 A possible reaction mechanism for the reaction of ethanedial with a reactive hydroxyl group of one of the NCP's in the fibre. Because ethanedial is dissolved in water it is present in its hydrolyzed form, containing four hydroxyl groups that are available to react. The end product of the above reaction is a hemi-acetal, further reaction of the

hydroxyl groups with another NCP chain would lead to the formation of a crosslinking acetal bond.

FTIR and NMR measurements were carried out to verify the possible modifications to the crystalline cellulose microfibrils. The spectra obtained from both techniques did not show evidence that one of the treatments alters the crystal structure nor the total degree of crystallinity of the fibres. Therefore, it was concluded that none of the treatments cause a degradation of the fibre's structural integrity.

The previous results indicate that treating flax fibres with ethanedial improves the mechanical properties of the NCP's without degrading the structural components of the fibre. This opens perspectives to extend the linear elastic response region of flax fibre reinforced polymers. Future work should focus on unravelling the deformation mechanisms acting in flax fibres. This will allow to propose targeted treatments to influence these mechanisms. Finally, the stability of the produced effects in humid environments must be evaluated. Otherwise the effect of the treatments could be nullified by moisture absorption.

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